Assessment of a computationally efficient protocol for the study of adsorption complexes in zeolites

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Introduction

Catalytic conversions in acidic zeolites such as H-ZSM-5 find applications in a whole range of industrial production processes. Unraveling the entire network of reactions taking place inside the zeolite pores, however, can be a very challenging task. In recent years, theoretical modeling has proven to be a highly useful tool to complement experimental studies in gaining a deeper understanding of such complex reaction mechanisms. Theoretical methods allow to establish if suggested reaction cycles can really occur in the zeolite pores, using calculated intrinsic barriers and rate coefficients of the elementary steps [1,2]. Before any reactions can take place the reactants have to adsorb onto specific active centers inside the pores. An additional enthalpy difference is associated with this preceding adsorption step, and this is inevitably included in experimentally measured reaction barriers. To compare results from theoretical studies with experimental values, the heat of adsorption should hence be accounted for, and an accurate representation of the pre-reaction complexes is indispensable [3].

In this work, a computationally efficient method that was previously successfully employed to study the thermochemistry and kinetics of elementary reactions, is used to model a series of adsorption complexes. Experimentally determined adsorption enthalpies for the adsorbates considered in this study are available in literature [4]. We aim to test the ability of the computational method to reproduce accurate enthalpies of adsorption across a series of compounds, as this would bring within reach the prediction of apparent barriers and global rate coefficients of catalytic reactions.

Methodology and results

Two-layered ONIOM-calculations on a large MFI cluster - containing 46 tetrahedral atoms in total, 8 of which constitute the high level region - are used for geometry optimizations. A conformational analysis is performed to identify the most stable adsorption complexes. Energies of the optimized states are further refined by single point calculations on the entire structure. In addition to pure B3LYP calculations, corrections to include long range dispersion interactions by means of an empirical potential of the form C_6R^{-6} [5], were also evaluated.

Table 1 Enthalpy of adsorption (kJ mol^{-1})

	experimental[a]	B3LYP[b]	B3LYP-D[b]
water	-90 ± 10†	-54.7	-77.3
methanol	-115 ± 5†	-56.8	-91.2
ethanol	-130 ± 5†	-56.4	-102.0
propanol	-145 ± 5†	-57.7	-119.9
trifluoroethanol	-90 ± 5‡	-48.6	-101.4
diethyl ether	-135 ± 5†	-61.5	-152.6
acetonitrile	-110 ± 5†	-57.2	-88.3
propionitrile	-120 ± 5†	-53.3	-101.4
butyronitrile	-145 ± 5†	-55.8	-120.2
isobutyronitrile	-130 ± 5†	-52.3	-115.0
chloroacetonitrile	-110 ± 5†	-33.3	-81.7
trichloroacetonitrile	-75 ± 5‡	-26.0	-90.1

[a] TPD measurements at 400K† or 350K‡ [4] [b] appropriate thermal corrections were added to electronic energies

Our results show that the pure DFT method (which lacks a proper description of dispersion interactions), is inadequate to determine the enthalpy of adsorption, yielding approximately the same value irrespective of the size of the adsorbate molecule. While theoretical estimates obtained with the extended cluster model quantitatively still underestimate the experimental adsorption enthalpies by about 20 kJ mol^{-1}, the qualitative outcome is significantly improved when the empirical corrections for the van der Waals interactions are taken into account and the experimentally observed trend in adsorption enthalpies is reproduced quite well.

References

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